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Geochemical analysis and petrochemical features of salt rocks from Middle and Upper Famenian saliferous formation of the Prypiat Through

Analiza geochemiczna i cechy petrochemiczne skał solnych środkowo- i górnofameńskiej formacji solonośnej w Zapadlisku Prypeci

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Abstract

The specific feature of the Pripyat Trough (paleorift) is presence of the continental crust in the basin basis. Intensity and direction of the processes in the Earth's crust led to creation of the depression structure. In this structure (basin), the salt formation with potassium salts sedimented during Middle-Upper Famen. Sedimentary rocks of the trough salt formations are represented by the difficult combination of chemogenic-terrigenous and salt rocks in the cross-section. Geochemical and structural-material features of the potash-bearing subformation salt rocks are considered in the article.

Key words: Pripyat paleorift, halite, sylvine, carnallite, bromine

Streszczenie

Specyficzną cechą Bruzdy Prypeci (paleorifu) jest obecność skorupy ziemskiej w podłożu basenu. Intensywność i kierunek procesów w skorupie ziemskiej doprowadziły do powstania struktury depresyjnej, w której sedymentowały osady. W strukturze (basenie) formacja solonośna z solami potasowymi sedymentowała w środkowym i górnym Famenie. Skały osadowe reprezentowane są przez skomplikowaną serię ewaporatową. Cechy strukturalne i geochemiczne potasowej subformacji zostały opisane w tym artykule.

Słowa kluczowe: paleoryft Prypeci, halit, sylwin, karnalit, brom

Introduction

Sedimentary rocks infilling the Pripyat potassium-bearing basin build a complicated natural system that during its development experienced the influence of a wide variety of processes. The Mid-Upper Famennian chloride saliferous formation (Figure) is composed of two subformations different in their properties: the halite (lower) and the potassium-bearing (upper) ones (Kaliynyye, 1984). Structure and evolution features of the potassium-bearing subformation suggest that its formation mechanisms contributed to the potassium scattering and were responsible for a specific distribution of potassium-bearing deposits in the section: the sites of potassium salt accumulation migrated in accordance with the structure modification. The potassium ore genesis during the Middle-Upper Famennian epoch is considered as a product of combined processes forming the red-colored and variegated hyper-saline associations in potassium deposits.

Materials and methods

Results of studies of the material composition and structural and textural features of saline rocks and of potassium deposits were summarized, systematized and examined with the identification of effects of postsedimentation processes.

The degree, nature and structure of the rock variability in the context of their geochemical analysis depend on the scrutiny and degree of generalization of the geological and mining parameters. The following different hierarchy levels have been consecutively considered: mineral –> mineral aggregate –> exploration borehole network –> geological block

Table 1. *Average chemical composition of the rock salt from the Middle-Upper-Famennian saliferous formation of the Pripyat potassium-bearing basin*

Tabela 1. Średni skład chemiczny soli kamiennej z środkowo o górnofameńskiej formacji potasonośnego basenu Prypeci.

Rock salt	**Number of Samples**	**Component Content, mass %**							**R_{Br}**
		KCl	NaCl	$MgCl_2$	$CaCl_2$	$CaSO_4$	Br	IR (Insoluble residue)	
Rock salt (halite subformation)	300	0.03	98.72	0.02	0.05	0.66	0.0063	0.38	42
Rock salt (potassium-bearing subformation)	500	0.23	94.78	0.04	0.05	0.51	0.0194	3.72	72
Coarse-crystalline sedimentary rock salt (potassium-bearing subformation)	12	0.03	99.35	0.05	0.04	0.12	0.0172	0.16	64
Giant crystalline rock salt (potassium-bearing subformation)	12	0.02	99.76	0.04	0.04	0.02	0.0233	0.06	86
Blue halite	10	0.55	97.80	0.19	0.01	0.77	0.0270	0.06	100
Red sylvinites micro-fine-grained	41	83.25	12.40	0.10	0.07	0.75	0.0383	3.35	32
Red sylvinites fine-mid-grained	52	77.27	21.23	0.09	0.08	0.46	0.0775	0,81	68
White sylvinites red colored hypersalt associations	11	92.18	7.40	0.08	0.06	0.11	0.2377	0.17	182
Milky-white sylvinites variegated hypersalt associations	9	82.81	16.94	0.13	0.01	0.09	0.3071	0.02	260
Carnallite	23	27.18	1.58	32.87	0.15	0.15	0.2930	0.64	143

–> deposit –> subformation –> formation. The study of each level variability has its peculiar features. In accordance with the model type used to simulate such variability the methods for its analyzing are conventionally subdivided into two groups: the geological and the mathematical ones.

There is a model used to discuss the bromine distribution among the chloride minerals. This model is based on the changeless of sea water composition and knowledge of bromine distribution coefficients between the chloride minerals and the liquid phase. This model is fully applicable for a restricted area of the sea water evaporation only. The bromine behavior was described quite fully in a wide variety of potassium accumulation processes. Bromine relationships should be considered in a context of geological and petrographical factors, affected a rock. Thus, according to the metamorphization theory, bromine content is not changed due to the hydrocarbonate water or clay material, but any inflow of chloride-calcium waters causes changes in the bromine-chlorine equilibrium of water-salt system.

When constructing the model the authors used, first of all, the geochemical indicators of potassium salt genesis and the theory of physical and chemical analysis of salt systems. A new principle to estimate the formation staging with the genetic plot developed by authors was the assumed possible jointed primary crystallization of sylvite and carnallite (Petrova, 1999).

The bromine distribution in salt minerals and rocks as well as the trace element distribution in chemogenic-terrigenous rocks of the Middle-Upper Famennian saliferous formation both in the section and over the whole area of the Pripyat Trough are examined. To assess the nature of bromine content variation in salt rocks of different composition the bromine formula/index was used $R_{Br} = \frac{Br_{fact}}{Br_{norm}}$, which is the ratio of actual bromine content in a rock (Br_{fact}) and the specific characteristic level – the bromine content at the lower boundary of carnallite crystallization zone (Br_{norm} – *op. cit.*).

The mathematical methods of data processing enabled to develop the principles of geological and genetic models. These models combined the use of geochemical indicators of salt rock genesis with various structural and textural features, the morphostructural characteristics of the ore bodies (potash deposits) and estimation of the distribution patterns of useful mineral components and impurities.

Discussion results

The bromine study in the salt minerals allows consideration of this element distribution in chloride minerals from different rock types. Bromine content of halite and sylvine is usually lower than that of corresponding stage of the normal or metamorphized sea water thickening (Lupinovich et al. 1976).

The rock salt of the halite subformation is monomineral (98.70%). $CaCl_2$, $CaSO_4$ and unsoluble residue characterize with the greatest variability. The calcium chloride is not determined in most samples. The average bromine content of rock salt is 0.0063%. Magnesium chloride and bromine have

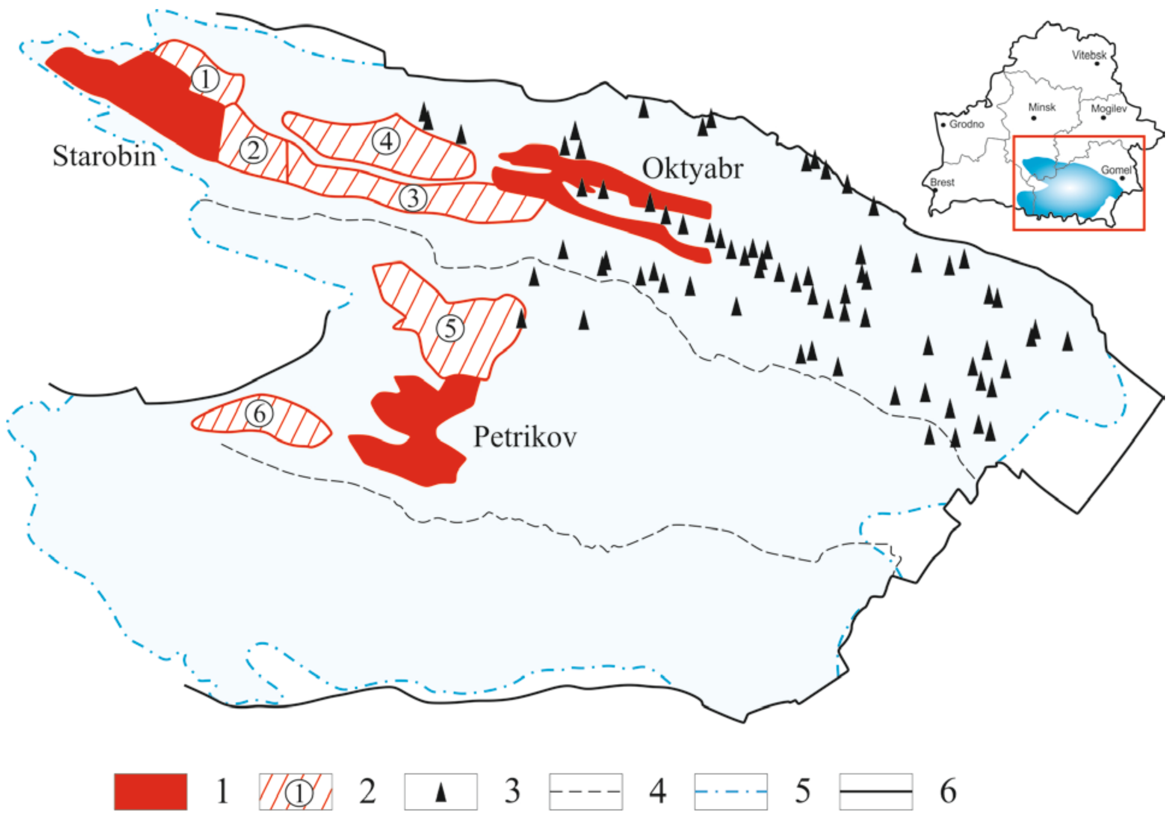

Figure 1. *Schematic location of the oil and potassium salt deposits*
1 – potassium salt deposits; 2 – potassium salt prospects (1 – Darasino, 2 – Nezhin, 3 – Smolovka, 4 – Ljuban, 5 – Drozdovo, 6 – Kopatkevichi, 7 – Zhitkovichi); 3 – oil deposits; boundaries of: 4 – structural areas, 5 – widespread occurrence of saliferous deposits; 6 – superregional trough-forming faults
Ryc. 1. Schematyczna lokalizacja złóż ropy naftowej i potasu
1 – złoża soli potasowych, 2 – perspektywiczne złoża potasu (1 – Darasino, 2 – Nezhin, 3 – Smolovka, 4 – Ljuban, 5 – Drozdovo, 6 – Kopatkevichi, 7 – Zhitkovichi), 3 – złoża ropy naftowej; granice: 4 – jednostek strukturalnych, 5 – występowania złóż solonośnych, 6 – regionalnych uskoków

the similar variation coefficients (84.5% and 87.9%, respectively). The model of evaporating sea water suggests that the first halite crystals (the precipitation beginning) should contain 0.0075% bromine (Kaliynyye, 1984).

The bromine amounts in halite of the potassium subformation (variation range from 0.011% to 0.021%) enabled the determination of its variation range in the sections of the rhythmic members and of the levels corresponding to the maximum salt water (brine) concentration in the Pripyat salt basin. The similarity of bromine content in the section of rhythmic members of potassium-bearing subformation from the in the northern and central parts of Pripyat trough suggest large brine reserves, as well as the similar type and nature of conditions existed there for a long time and created brines of specific composition. Increased amounts of this element were confined to rock salt beds underlying the potash horizons. The monomineral fractions of the zonal halite (a primary variety) and spathic halite (a diagenetic variety) isolated from the same rock salt sample showed that the bromine content in an altered mineral is 1.2-1.5 times higher. The maximum bromine content was determined in a blue halite (Table).

Sylvinites of the Mid-Upper Famennian subformation were described by significant variation ranges of the indicative element concentrations and deviations of their contents from the normal ones (ex. from 0.0385 to 0.4121% for bromine). This element content depends on structural and textural features of sylvinites and their color, which is again indicative for bromine distribution controlled by the crystallization processes. There was observed a distinct tendency of bromine content increase from the dark-colored to light-colored mineral varieties and from the fine-grained to coarse-grained mineral varieties (R_{Br} grows from 50 to 90). The maximum content was registered in white sylvinites, especially, being combined with the blue halite (R_{Br} = 277) They typically occur in potassium deposits of the variegated hyper-saline association, as well as in some sections of the red-colored association (R_{Br}= 146). Bromine content in sylvinite of this variegated variety is often equal to that of carnallite. Bromine content in the red-colored sylvinite varies widely but usually it is below its normal level. The bromine index for sylvine there is usually smaller than in coexistent halite. In the colorless sylvinites the reversed correlation is observed: the bromine index in sylvine is usually higher than in halite (Petrova et al., 1985).

An increase of magnesium chloride in the solution reduces solubility of the potassium chloride – the sylvite sediments. The sylvinite formation could be a decomposition product of the primary carnallite or sylvine deposits. The appearance of calcium chloride instead of $MgCl_2$ in the solution will further decrease the halite solubility and slightly increase that of potassium chloride. Such brines will be able to release the carnallite. Due to dissolution of carnallite and sylvite-carnallite rocks, the leaching brines often are not associated with the material redeposition *in situ*. These brines can be transported and mixed with the normal basin waters.

A low bromine content of micro- and fine-grained red sylvinites as well as presence of primary sedimentary structures indicated the brine composition change at the sedimentation stage: a widespread effect of the redeposition-dissolution processes. The more rocks are dissolved, the more solution is saturated with the potassium chloride, then bromine content in sylvine sharply decreases and the bromine index value is 40–50.

Three groups of mineralogical and petrographic features identified with a certain degree of conventionality are indicative for development of postsedimentary processes. Dissolution and recrystallization processes, accompanied by the lightening, bleaching, grain growth, formation of fluidal structures and textures are the most important among them. The fluidal textures and other phenomena refer to those lithological deformation features that occur in any salt rock (rock salt, sylvinite, carnallite) regardless the depth of their occurrence and show a local areal extent.

Absolute values of bromine content in all studied carnallite samples are within the normal values, and R_{Br} ranges from 110 to 190.

Conclusion

Several thousand chemical analyses of Mid-Upper Famennien evaporites in the Pripyat through evidenced that:

- the bromine content in halite is mainly characteristic for the thickening stage;
- the bromine content in carnallite shows the similar values in all potash deposits and it is comparable with world salt formations, in spite of factors diversity that influenced on formation of saliferous strata, the power and duration of such influence, and the absence of completely analogous types of geological minable deposits. After authors' opinion, this, on the one hand, evidently suggests an obvious carnallite priority and on the other hand, can serve as an indisputable argument for the stability of sea water composition in the Phanerozoic;
- the bromine content of the sylvine varies considerably depending on its formation conditions: from the predominantly synsedimentary accumulation in the salt basin itself at slightly different stages of the pegnitogenic process (with a subsequent influence of postsedimentary agents or factors) to the penetration of waters from the enclosing rocks into salt strata, which were aggressive to sylvinite and other potassium salts. In addition, if at the halite precipitation stage the temperature fluctuations do not affect the mineral formation, then at the potassium stage the temperature regime can be a determining factor. The normal and nearly theoretical bromine content in the sylvine is combined with the continued tendency of this element variations depending on its color intensity and a grain size.

There are various concepts of possible conditions of the potash deposits formation and their further geological evolution in the Pripyat potassium-bearing basin, which concern not only the details, but also the fundamental nature of salt mother brine origin.

The formation models of red-colored and variegated hyper-saline associations are examined on the basis of their structural-material parameters and prevailing spatial development. The basic principles of developed models are as follow: 1) structural and material priority; 2) ascendant and descendant mechanisms of the element recurrence in the sedimentary cycle; 3) separation of the solid and liquid phases; 4) interrelation between the chemical composition of all non-salt rock complexes indicating the existence of integration mechanisms of deposit formation within the basin.

It was shown that the appearance of the deposits of red-colored hyper-saline association was described by the recurrence and clear differentiation of the section-forming elements within the horizon, the presence of banded sylvinites, Their formation was significantly influenced by processes of primary sylvine crystallization from the descendant solutions.

The retrospective conceptual geological-genetic model of the formation of variegated hyper-saline association is based on the reassessment of the importance of sedimentary processes and mechanisms and post-sedimentary transformations of potassium and potassium-magnesium rocks. To explain the genesis and formation conditions of potassium-bearing halogenic systems, a model based on the simultaneous sylvine and carnallite precipitation was proposed. It was assumed that deposits of sylvine-carnallite composition were initially accumulated at the level of physical-chemical system transition. Then process of incongruent carnallite decomposition under the influence of solutions with different composition and salinity and change in the boundaries of solid phase fields with temperature fluctuations led the light-colored (milky-white) sylvinite formation.

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